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(54) Process for the catalytic epoxidization of olefins with hydrogen peroxide

(57) A process for the catalytic epoxidization of olefins by reaction with hydrogen peroxide according to the double phase technique with onium salts, wherein the reaction is conducted in a liquid aqueous-organic two-phase system consisting of:

- a) an organic phase substantially containing the olefin and
- b) an aqueous acidic phase substantially containing the hydrogen peroxide,

in the presence of a catalytic system consisting of at least one element or a derivative thereof selected from W, Mo, V and of at least one derivative of P or As.

SPECIFICATION

Process for the catalytic epoxidization of olefins with hydrogen peroxide

- 5 The present invention relates to a process for the catalytic epoxidization of olefins with hydrogen peroxide by a catalytic oxidation reaction in a liquid phase. More particularly, the invention relates to a process for the preparation of epoxides by the oxidation of olefins in a liquid phase with hydrogen peroxide in the presence of a catalytic system based on transition metals, by using the reaction technique called "phase transfer". 5
- The compounds obtained by the process of the invention, epoxides of olefins, are chemical products of considerable industrial importance. In fact, they represent products that find application in industry, on a high qualitative scale, within a wide range of uses. Besides being useful as intermediates in organic syntheses, amongst the main uses there may be noted those in which they are employed as intermediates in the production of urethanes, and in the production of blown or foamed products, of glycols for lubricants, surfactants, esters for plasticizers, polyester resins, etc. The epoxides are also used directly in the preparation of thermosetting epoxy resins. 10 15
- Quite a number of processes for epoxidization of olefins are known, although most are methods which either did not find a practical industrial application or are now no longer of interest because of for example economical or ecological reasons.
- Thus, at present, apart from the direct oxidation of ethylene to ethylene oxide, propylene oxide and epoxides in general are obtained almost exclusively by the known chlorohydrin process. 20
- Schematically, this process comprises reacting an olefin with chlorine water obtaining thereby the chlorohydrin which is treated with alkali (lime) thereby obtaining the corresponding epoxide. However, this process has economic and environmental disadvantages as it leads to the production of both mineral as well as organic chlorinated byproducts which, while by themselves not exploitable, present problems in respect of the qualitative and quantitative disposal thereof. To this must be added the increasing cost of chlorine. 25
- Therefore, quite recently interest has been shown in an epoxidization process conducted in an anhydrous organic phase of an olefin with an organic hydroperoxide in the presence of catalysts based on molybdenum, tungsten and vanadium.
- Nonetheless, the production of epoxide is accompanied, in quantities equivalent to or even greater than the epoxide, by the production of the alcohol corresponding to the hydroperoxide, the exploitation or recycling of which represents a serious economical disadvantage of this process. 30
- There have been developed epoxidization processes by means of molecular oxygen with silver catalysts, which, however, have had a success limited to ethylene; the corresponding techniques proved to be not extendible to other olefins of interest (i.e. propylene).
- Hydrogen peroxide, because its oxidizing action causes no environmental or pollution problems, has been suggested as being suitable for a certain number of epoxidization processes. 35
- According to these processes, since the activity of the hydrogen peroxide towards the olefins as such is rather limited or altogether absent, it is necessary to use activating agents, in general organic acids such as formic acid or acetic acid in organic solvents, which acids, in the form of peracids, form *in situ* the reactive epoxidizing agent. 40
- These processes have not been very successful, both because of the difficulty of obtaining peracids as well as because of the instability of the epoxides in an acid medium which makes it necessary to utilize rather burdensome operational conditions.
- Other processes have been described as applicable selectively to the preparation of epoxy-alcohols (glycidols) by an epoxidation of hydrosoluble olefins with hydrogen peroxide, in an aqueous solution containing primary or secondary alcohols, and in the presence of catalysts based on Mo, V and W. 45
- However, this technique is substantially directed towards glycidols only, compounds that are of limited interest. On the other hand, the epoxidization reaction of the olefins with hydrogen peroxide leads to the formation of water which, especially when metal catalysts are used in the state of peroxides, inhibits with its accumulations the reaction itself. 50
- It has been attempted to overcome this drawback with the use of concentrated solutions of hydrogen peroxide, as well as by using catalytic systems.
- Thus, there have been described olefins oxidizable by reaction with highly concentrated hydrogen peroxide in a homogeneous essentially organic liquid phase, in the presence of soluble catalytic systems based on elements of the groups IV, V and VI B (Ti, V, Mo, W) of the Periodic Classification of Elements associated with elements such as Pb, Sn, As, Sb, Bi, Hg. 55
- The results thereof did not meet expectations on the practical level because of the slowness of the reaction and because of the expensiveness of the catalytic system, consisting in general of very sophisticated metalorganic compounds, necessary for their solubility in the organic medium.
- Moreover, the use of hydrogen peroxide of high concentration (>70%) involves some risks from the point of view of safety, not easily surmountable in an economical way. 60
- Improvements have been described as achievable by the use, in the above mentioned technique, of catalysts based on tungsten or molybdenum or arsenic or boron with an excess of olefin, in general in combination with continuous distillation of the interfering water.
- Here too is practically required the use of concentrated solutions (> 70%) of hydrogen peroxide, with the 65

corresponding handling problems, and also as already mentioned the safety of the installations. Moreover, the continuous removal of the reaction water, besides that introduced by the hydrogen peroxide itself, an operation that makes practically necessary from the start high H_2O_2 concentrations, is particularly burdensome with regard to the economy of the process.

- 5 On the other hand, the oxidation of olefins with hydrogen peroxide involves an intrinsic contradiction given by the operational conditions which require at best an aqueous medium, possibly acid, as far as the catalytic system and the hydrogen peroxide are concerned, while the oxidization reaction and the stability of the epoxide require preferably a neutral organic medium. 5

All the above discussed known techniques using hydrogen peroxide tend to make the reaction medium homogeneous in some way and also tend to avoid the inhibiting accumulation of H_2O , with rather uncertain results, at least from the point of view of the actual industrial workability of such processes. 10

The present invention provides a process for the catalytic epoxydization of olefins by reaction with hydrogen peroxide according to the double phase technique with onium salts, wherein the reaction is conducted in a liquid aqueous-organic two-phase system which comprises (a) an organic phase 15 substantially containing the olefin and (b) an aqueous acidic phase substantially containing the hydrogen peroxide, in the presence of a catalytic system comprising a first catalytic component which is at least one first element or a derivative thereof selected from tungsten, molybdenum and vanadium, and a second catalyst component which is at least one derivative of phosphorus or arsenic. 15

Thus there is provided a process for catalytic epoxidation of olefins, using as an oxidizing agent hydrogen peroxide, that is easy and economic to carry out and which is generally free of the drawbacks of the above described prior art processes. 20

In particular, the process of the invention may be carried out with dilute hydrogen peroxide, and may have a high selectivity for the desired epoxide which is obtained by means of an efficient long-life catalytic system, without it being necessary to carry out a burdensome continuous distillation of the reaction water.

25 These advantages are generally obtained by conducting the reaction in a double aqueous-organic liquid phase. 25

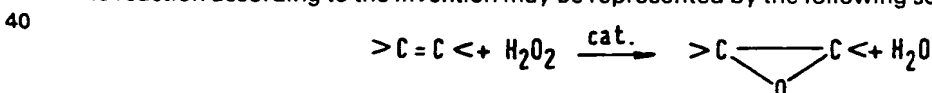
This technique involves the use of two unmixable or hardly mixable reaction means of differing polarity, so that the pH control as well as the concentration of the hydrogen peroxide and the elimination of the reaction water has proved substantially less inhibiting of the effectiveness of the process.

30 It is quite well known to conduct chemical reactions in general, substantially based on ionic exchange, according to the so-called double phase technique. 30

There has also been described the possibility of epoxydizing olefins with hydrogen peroxide, in a double phase, in the presence of mineral derivatives based on tungsten and molybdenum. Nevertheless there has not been any practical interest in this method because of the poor efficiency of the catalyst.

35 It has now been found, according to the invention, that the epoxydization reaction with hydrogen peroxide of olefins, catalyzed by compounds based on transition metals, may be effected by the use of a particular catalytic system which, unexpectedly increasing the epoxydization reaction, allows epoxydization of olefins to be conducted in an economical and operationally easy way, according to the double phase technique. 35

The reaction according to the invention may be represented by the following scheme:



The reaction, as stated above, is conducted in a double phase, aqueous-organic system, preferably with vigorous stirring in the presence of the above defined catalytic system. The organic phase consists of the olefin and possibly an organic solvent and the aqueous phase from the hydrogen peroxide. 45

The temperature and the operational pressure are practically determined by the reactivity and by the nature of the olefin, and by the stability of the hydrogen peroxide and the onium salts used in the organic medium.

50 Temperatures from 0°C to 120°C and pressures between atmospheric pressure and about 100 atmospheres shall be considered, as a rule, sufficiently operative. 50

The olefins that may be subjected to the epoxydization reaction, according to this invention, may be represented by the following formula:



60 wherein R_1 , R_2 , R_3 and R_4 , optionally substituted with functional groups inert to the reaction conditions, each represent a hydrogen atom or a hydrocarbyl group such as an alkyl or alkenyl group having up to 30 carbon atoms, a cycloalkyl or cycloalkenyl group having from 3 to 12 carbon atoms, optionally branched, or aryl, alkyl-aryl or alkenyl-aryl group having from 6 to 12 carbon atoms; moreover, an R_1 , R_2 , R_3 , R_4 group taken together with an adjacent group may represent an alkyl or alkenyl group having from 1 to 12 carbon atoms in the resulting cycle. The expression "hydrocarbyl group" used herein means a radical derived from a 65

hydrocarbon.

Substituent functional groups, inert to the reaction conditions, are, for instance, halogens (Cl, Br, F, I), and hydroxyl, nitro, alkoxy, amino, carbonyl, carboxylic, esteric, amido and nitrile groups.

As indicated above, the R_1 , R_2 , R_3 and R_4 groups may also be alkenyls, in other words the process according to the invention is applicable also to polyolefins such as dienes and trienes, whether conjugated or not.

Olefins suitable epoxidization according to the invention include, by way of example, alkyl, alicyclic and alkylaryl unsaturated hydrocarbons having up to 20 carbon atoms, such as propylene, butenes, pentenes, and in general the linear or branched mono- and di-olefins having up to 20 carbon atoms, cyclohexene, norbornene, limonene, camphene, vinyl-cyclohexene, styrene, indene and stilbene, unsaturated alkyl halides such as allyl halides, unsaturated acids and their esters such as acrylic, methacrylic, crotonic and oleic acid, unsaturated alcohols and their esters such as allyl alcohol, and unsaturated aldehydes and ketones such as methylallyl acetone.

Definitely acid pH values increase the stability of the hydrogen peroxide, but makes the epoxide unstable. Thus, convenient pH values are those from 2 to 6. Such a range of pH values is obtained in practice directly by the presence of the system consisting of the reactants and of the catalyst used, or, if necessary, it may be adjusted for this purpose with mineral acids (e.g. HCl).

On the other hand, as already indicated above, the adopted double-phase reaction technique renders the operation of the process less sensitive to occasional variations in the pH value.

The duration of the reaction depends on the nature and on the quantity of the catalyst, on the solvent medium and on the olefin used in the process. In general, times comprised between just a few minutes and several hours will be sufficient for completing the reaction.

The quaternary onium salts used in the process are known salts that may be represented by the formula: $(R'_1, R'_2, R'_3, R'_4 M)^+ X^-$, wherein M is a pentavalent element belonging to Group V A of the Periodic System, X^- is a stable anion such as Cl, Br, HSO_4^- , NO_3^- , and R'_1 , R'_2 , R'_3 and R'_4 each represent monovalent hydrocarbyl groups having a total number of carbon atoms of up to 70, but preferably from 25 to 40.

Depending on whether M is an atom of N, P, As or Sb, there is obtained the corresponding onium salt, i.e. the ammonium (N), phosphonium (P), arsonium (As) or stibonium (Sb) salt.

The catalytic system suitably comprises, in accordance with the invention, a first catalyst component which is at least one element or at least one of its mineral, organic or metalorganic derivatives selected W, Mo and V, but preferably W capable of being transformed *in situ* and under the reaction conditions into a compound or a species catalytically active.

Derivatives of such elements, having such characteristics, are the oxides, mixed oxides or salt-oxides, oxy-acids, homopolyacids and their salts, heteropoly-acids (silicon-molybdic acid, silicon-tungstic acid etc.) and their salts, salts derived from mineral hydrogen-acids (e.g. HCl), naphthenates, acetylacetonates and carbonyl derivatives thereof.

Effective derivatives that are considered to be particularly effective are, besides the elements W, Mo and V as such, the tungstic, molybdic and vanadic acids and the corresponding neutral salts or acid salts of alkali and alkaline earth metals, the metal-carbonyls $W(CO)_6$, $Mo(CO)_6$, the oxides MoO_2 , Mo_2O_5 , Mo_2O_3 , MoO_3 , WO_2 , W_2O_5 , WO_6 , VO_2 , V_2O_3 , V_2O_5 , the sulphides WS_2 and WS_3 , the oxychlorides, the chlorides, the naphthenates and the stearates of molybdenum, tungsten and vanadium.

The second component of the catalytic system suitably comprises, in accordance with the invention, at least one mineral, organic or metalorganic derivative of phosphorus or arsenic, capable of forming, under reaction conditions, an association catalytically active with the first, previously defined catalyst component.

Derivatives having such characteristics are the oxides, oxyacids and their salts, sulphides and salts derived from hydrogen acids (e.g. HCl), the compounds of formula $R''_1 R''_2 M(=O)X$ and $R''_3 M(=O)XY$, wherein M is P or As and R''_1 , R''_2 and R''_3 each represent a hydrogen atom or an alkyl, cycloalkyl, aryl or alkylaryl group having up to 12 carbon atoms, and wherein X and Y each represent hydrogen, a hydrocarbyl group (e.g. an alkyl or an aryl group), a halogen (e.g. chlorine), a hydroxyl, alkoxy or carboxylic group, or a mineral oxyacid.

Particularly effective derivatives are considered to be phosphoric, phosphorous, polyphosphoric, pyrophosphoric, phosphonic, arsenious, arsenic and arsonic acids and their alkaline salts, the oxides P_2O_3 , P_2O_5 , As_2O_3 , As_2O_5 , the oxychlorides, the fluorides and the chlorides of phosphorous and arsenic.

The two or more catalyst components used in the process may belong to different molecules or they may be part of the same complex molecule that incorporates them.

In this case there may be used heteropolyacids such as phosphotungstic, arsenotungstic, phosphomolybdic heteropolyacids or their alkali or alkaline earth salts.

These may easily be obtained by heating and acidifying a solution, for instance consisting of a tungstate and of a salt of the central atom of the complex in the appropriate state of oxidization, according to known methods.

Analogously, the compounds of formula:



as defined above are either commercially available or may be prepared by means of known techniques.

The two or more components of the catalytic system may be suitably used in a mutual atomic ratio, expressed as the total of the metal or metals belonging to the first catalyst component with respect to the total of the metal or metals belonging to the second catalyst component, of from 12 to 0.1, more preferably from 1.5 to 0.25.

- 5 The catalytic system is, moreover, preferably used in an amount of from 0.0001 to 1 g-atom of metal or of total metals belonging to the first catalyst component per 1 mol of hydrogen peroxide, more preferably from 0.005 to 0.2 g-atom per 1 mol of hydrogen peroxide. 5

There may be used as indicated above mixtures of catalyzing elements and/or their derivatives thereof within the composition of the catalytic system.

- 10 The amount of quaternary onium salt present in the heterogeneous system may vary within wide limits. At any rate, there may be achieved effective results by using from 0.01 to 2 mols of onium salt per 1 g-atom of catalyst, more preferably from 0.1 to 1 mol per 1 g-atom, relative to the first catalyst component or to the sum of the first catalyst components. 10

- Effective onium salts have proved to be dicetyldimethylammonium chloride and tricaprylmethylammonium chloride. 15

The reactants are preferably used according to substantially equimolecular ratios, but a limited excess or lack of one reactant with respect to another is not detrimental to the course of the reaction.

For indicative purposes, workable operational values may be considered to be from 0.1 to 50 mols of olefin per mol of hydrogen peroxide, more preferably from 1 to 20 mols of olefin per mol of hydrogen peroxide.

- 20 The reaction is conducted, as previously indicated, according to the double-phase technique. More particularly, the organic phase (a) may comprise the reacting olefin itself, used in a suitable excess, or it may comprise the reacting olefin dissolved in a suitable organic solvent. 20

- As solvents for the organic phase are used inert solvents substantially unmixable with the aqueous phase; effective practical results are obtained by the use of aliphatic, alicyclic and aromatic hydrocarbons such as heptane, octane, cyclohexane, benzene, toluene, and xylenes, chlorinated hydrocarbons such as dichloromethane, trichloromethane, chloroethane, chloropropane, dichloroethanes, trichloroethanes, tetrachloroethanes, di- and trichloropropanes, tetrachloropropanes and chlorobenzene, alkyl esters such as ethyl acetate or suitable mixtures thereof. 25

- The choice of the type of organic phase (a) will depend on the reactivity of the starting olefin and on the parameters used in each instance. In the case that in the organic phase there is used an above described inert solvent, the concentration of the olefin in the solvent is not critical for the performance of the process. 30

Operational values for the olefin concentration in the organic phase are preferably from 5% to 95% by weight; higher values or lower values are, however, compatible within the limits of their practicability. The concentration of hydrogen peroxide in the aqueous phase may be suitably from 0.1 to 70% by weight.

- 35 Nevertheless, the process according to the invention offers the advantage of allowing to work with low concentration values of the hydrogen peroxide. Effective concentration values of the hydrogen peroxide have proved to be from 1% to 10% by weight; values below 1% have also proved to be workable. This brings with it the favourable economical aspects of the process, when compared with the costly preparation of solutions with concentrations greater than 70% known from the prior art, as well as when compared with the necessity of maintaining such high concentrations during the process while carrying out the safety aspects already mentioned. 40 40

A practical way of conducting the process of the invention is as follows.

- Into a reactor fitted with a stirrer and a heat controlling system and a reflux coolant, there are introduced in pre-established quantities and ratios, the reactants (H_2O_2 and the olefin in the solvent). Thereupon there is introduced the catalytic system and the rest of the solvent, with the onium salt in the desired quantities. Under vigorous stirring, the heterogeneous mixture is brought to the reaction temperature for the desired time. At the end, after separation of phases and cooling, the epoxide and the reactants are separated by means of conventional methods (e.g. distillation). 45 4

The process is particularly convenient to conduct because of the mild and simple operational conditions.

- 50 More particularly, the process may be operated effectively using a high olefin concentration in a solvent medium, or in the absence of a solvent. 50 5

- In the previously known processes which do not describe the use of solvents and which are conducted in a homogeneous phase with concentrated H_2O_2 , there are prescribed large excesses of the starting olefin, necessary for ensuring reasonable margins of operational safety. This circumstance is not relevant in the case of the process according to the invention, in which, on the contrary, the safety aspect is overcome by means of the double-phase technique. 55 5

Still other advantages may be seen in the possibility of using hydrogen peroxide at a low concentration, which may be easily and economically retrieved or may be easily prepared without involving operational security risks.

- 60 Lastly, the high yields and high selectivity that are obtainable together with the above indicated advantages ensure that the process will have considerable industrial application. 60 6

The invention will be further described with reference to the following illustrative examples. Examples 4, 6, 18 and 19 are given for comparative purposes. The symbol w/v stands for weight/volume.

Example 1

Into a four-necked flask, fitted with a stirrer, a thermometer and a reflux-coolant, there were introduced 22.1 g of octene-1 (0.197 mols), 0.8 g of tricaprylmethylammonium chloride (0.002 mols), 40 cc of H₂O, 1.65 g of Na₂WO₄·2H₂O (0.005 mols), 0.83 g of NaH₂PO₄·H₂O (0.006 mols), 2 cc of 14.7% concentration w/v of H₃PO₄ (0.003 mols), 10.96 g of 38.2% concentration H₂O₂ (0.123 mols), and 16 cc of 1,2-dichloroethane. Thereupon to the mixture was added 1.30 cc of H₂SO₄ at 31.7% concentration, and, under vigorous stirring, the mixture was rapidly brought up to 70°C and maintained at this temperature for 45 minutes. At the end of the reaction, from the reaction mass were dosed off iodometrically 0.0023 mols of unreacted H₂O₂ and by gas-chromatography (GLC) 0.102 mols of epoxyoctane, which corresponded to a conversion of hydrogen peroxide equal to 98.1%, with a selectivity with respect to epoxyoctane of 84.5%.

Example 2

Into a four-necked flask, fitted with a stirrer, a thermometer and a reflux-coolant, there were introduced 35.61 g of octene-1 (0.318 mols), 60 ml of benzene, 1.2 g of dicetyldimethylammonium chloride (0.002 mols), 40 ml of water, 3.3 g of Na₂WO₄·2H₂O (0.010 mols), 7.0 ml of 14.7% concentration H₃PO₄ (0.0105 mols) and 11.47 g of 38.2% concentration H₂O₂ (0.129 mols). This mixture was thereupon rapidly brought up to 70°C, under vigorous stirring, and was then maintained at that temperature for 2 hours. At the end of the reaction, from the reaction mass were dosed off iodometrically 0.0097 mols of unreacted H₂O₂ and by gas-chromatography 0.1014 mols of epoxyoctane, which corresponded to a conversion of hydrogen peroxide of 92.4%, with a selectivity with respect to epoxyoctane of 86.4%.

Example 3

Into a four-necked flask, fitted with a stirrer, a thermometer and a reflux-coolant, there were introduced 22.1 g of octene-1 (0.197 mols), 1.2 g of dicetyldimethylammonium chloride (0.002 mols), 40 cc of H₂O, 1.65 g of Na₂WO₄·2H₂O (0.005 mols), 0.83 g of NaH₂PO₄·H₂O (0.006 mols), 2 cc of 14.7% concentration H₃PO₄ (0.003 mols), and 10.96 g of 38.2% concentration H₂O₂ (0.123 mols). Thereupon there were added 0.95 cc of 31.7% concentration H₂SO₄ and, under vigorous stirring, the mixture was brought rapidly up to 70°C and was then maintained at this temperature for 45 minutes. At the end of the reaction, from the reaction mass there were dosed off iodometrically 0.006 mols of unreacted H₂O₂ and by liquid gas chromatography (LGC) 0.0936 mols of epoxyoctane, which corresponded to a conversion of hydrogen peroxide of 95%, with a selectivity with respect to epoxyoctane of 80%.

Example 4 (comparative example)

Example 2 was repeated, except that the H₃PO₄ was replaced by an equivalent quantity of H₂SO₄. After 2 hours of reaction, from the reaction mass were dosed off 0.0986 mols of unreacted hydrogen peroxide and 0.007 mols of epoxyoctane, which corresponded to a conversion of hydrogen peroxide of 23.5%, with a selectivity with respect to epoxyoctane of 23.2%.

Example 5

Into a four-necked flask, fitted with a stirrer, a thermometer and a reflux-coolant, there were introduced 22.1 g of octene-1 (0.197 mols), 0.8 g (0.002 mols) of tricaprylmethylammonium chloride, 40 cc of H₂O, 1.65 g of Na₂WO₄·2H₂O (0.005 mols), 3.12 g (0.010 mols) of Na₂HAsO₄·7H₂O, 10.96 g (0.123 mols) of 38.2% concentration H₂O₂, and 16 cc of 1,2-dichloroethane. Thereupon there were added about 3 cc of 31.7% concentration H₂SO₄ and, under vigorous stirring, the mixture was rapidly brought up to 70°C and maintained at this temperature for 45 minutes. At the end of the reaction, from the reaction mass were dosed off 0.0047 mols of unreacted H₂O₂ (conversion 96.2%) and 0.0978 mols of epoxyoctane (selectivity 82.6%).

Example 6 (comparative example)

Example 5 was repeated, but in the complete absence of tungstates, using 240 ml of 31.7% concentration H₂SO₄. After 60 minutes of reaction, from the reaction mass there was dosed off a quantity of H₂O₂ equal to that introduced initially. The LGC did not reveal the presence of any epoxyoctane.

Example 7

Example 1 was repeated, but using 0.93 g of hexacyltributylphosphonium chloride (0.002 mols) instead of the quaternary ammonium salt. After 60 minutes of reaction, from the reaction mass there were dosed off 0.0051 mols of unreacted H₂O₂ (conversion = 95.9%) and 0.0892 mols of epoxyoctane (selectivity = 75.6%).

Example 8

Example 2 was repeated, using as a catalyst 2.46 g of sodium phosphotungstate (0.010 g-atom of W) and by adding to the reaction system 1.9 ml of NaOH at 35% concentration. After 2 hours of reaction, as in Example 1, from the reaction mass were dosed off 0.0376 mols of unreacted hydrogen peroxide and 0.0568 mols of epoxyoctane, which corresponded to a conversion of the hydrogen peroxide of 70.8%, with a selectivity with respect to epoxyoctane of 62.1%.

Example 9

Into a four-necked flask, fitted with a stirrer, a thermometer and a reflux-coolant, there were introduced 31.1 g (0.379 mols) of cyclohexene, 0.6 g (0.001 mols) of dicetyldimethylammonium chloride, 40 cc of H₂O, 0.66 g (0.002 mols) of Na₂WO₄·2H₂O, 1.1 cc (0.0015 mols) of 14.7% concentration H₃PO₄, 10.96 g (0.123 mols) of 38.2% concentration H₂O₂, and 40 cc of benzene. This mixture, subject to vigorous stirring, was rapidly brought up to 70°C and maintained at this temperature for 15 minutes. At the end of this period, from the reaction mass were dosed off 0.009 mols of unreacted H₂O₂ and 0.096 mols of epoxycyclohexane, which corresponded to a conversion of hydrogen peroxide of 92.6%, with a selectivity with respect to epoxycyclohexane of 84%.

Example 10

Into a four-necked flask, fitted with a stirrer, a thermometer and with a reflux-coolant, there were introduced 16.2 g of cyclohexene (0.197 mols), 60 ml of benzene, 1.2 g of dicetyldimethylammonium chloride (0.002 mols), 40 ml of water, 3.3 g (0.010 mols) of Na₂WO₄·2H₂O, 4.62 ml of 14.7% concentration H₃PO₄ (0.0069 mols), and 11.47 g of 38.2% concentration H₂O₂ (0.129 mols). This mixture was then rapidly brought up to 70°C, under vigorous stirring, and was then maintained at this temperature for 30 minutes. At the end of the reaction, from the reaction mass were dosed off 0.015 mols of unreacted H₂O₂ and 0.099 mols of epoxycyclohexane, which corresponded to a conversion of hydrogen peroxide of 88.4%, with a selectivity with respect to epoxycyclohexane of 86.8%.

Example 11

Into a four-necked flask, fitted with a stirrer, a thermometer and a reflux-coolant, there were introduced 30.2 g (0.368 mols) of cyclohexene, 0.6 g (0.001 mols) of dicetyldimethylammonium chloride, 40 cc of H₂O, 0.66 g (0.002 mols) of Na₂WO₄·2H₂O, 1.1 cc (0.0015 mols) of 14.7% concentration H₃PO₄, and 11.2 g (0.126 mols) of 38.2% concentration H₂O₂. Under vigorous stirring the mixture was then brought up to 70°C and maintained at this temperature for 15 minutes (initially the reaction was exothermic). At the end of the reaction, from the reaction mass were dosed off 0.0057 mols of unreacted H₂O₂ (conversion = 95.5%) and 0.0985 mols of epoxycyclohexane (selectivity = 81.9%).

Example 12

Into a four-necked flask, fitted with a stirrer, a thermometer and a reflux-coolant, there were introduced 29.1 g (0.355 mols) of cyclohexene, 20 ml of 1,2-dichloroethane, 0.4 g (0.001 mols) of tricaprylmethylammonium chloride, 40 ml of water, 0.66 g (0.002 mols) of Na₂WO₄·2H₂O, 1.1 ml (0.0015 mols) of 14.7% concentration H₃PO₄ and 10.96 g (0.123 mols) of 38.2% concentration H₂O₂. The reaction mixture was then rapidly brought up to 70°C and maintained at this temperature for 45 minutes. At the end of this period, from the reaction mass were dosed off 0.004 mols of unreacted H₂O₂ and 0.099 mols of epoxycyclohexane, which corresponded to a conversion of the hydrogen peroxide of 96.7%, with a selectivity with respect to epoxycyclohexane of 83%.

Example 13

Example 10 was repeated, but using 4.9 ml of 14.7% concentration H₃PO₄ (0.0074 mols) and operating at 50°C. After a reaction time of 30 minutes, from the reaction mass were dosed off 0.037 mols of unreacted H₂O₂ and 0.0848 mols of epoxycyclohexane, which corresponded to a conversion of the hydrogen peroxide of 71.3%, with a selectivity with respect to epoxycyclohexane of 92.1%.

Example 14

Example 13 was repeated, except that the reaction time was increased to 1 hour. From the reaction mass were then dosed off 0.0122 mols of unreacted hydrogen peroxide and 0.0951 mols of epoxycyclohexane, which corresponded to a conversion of the hydrogen peroxide of 90.5%, with a selectivity with respect to epoxycyclohexane of 81.4%.

Example 15

Example 10 was repeated, but using 3.96 g of WCl₆ (0.010 mols) instead of Na₂WO₄·2H₂O and 3.58 g (0.010 mols) of Na₂HPO₄·12H₂O instead of H₃PO₄. To this reaction mass were then added 8.5 ml of 35% concentration NaOH. After 30 minutes of reaction, there were then dosed off 0.01057 mols of unreacted hydrogen peroxide and 0.0688 mols of epoxycyclohexane, which corresponded to a conversion of hydrogen peroxide of 91.6%, with a selectivity with respect to epoxycyclohexane of 55.9%.

Example 16

Example 10 was repeated, but using 3.52 g of W(CO)₆ (0.010 mols) instead of Na₂WO₄·2H₂O and 3.58 g (0.010 mols) of Na₂HPO₄·12H₂O instead of H₃PO₄. To this reaction mass were then added 2 ml of 31.7% concentration H₂SO₄. After 30 minutes of reaction, there was dosed off 0.00506 mols of unreacted hydrogen peroxide and 0.0565 mols of epoxycyclohexane, which corresponded to a conversion of the hydrogen peroxide of 96.1%, with a selectivity with respect to epoxy-cyclohexane of 43.6%.

Example 17

Example 10 was repeated, but using 4.4 ml of 14.7% concentration H_3PO_4 (0.0066 mols), and operating at a temperature of 50°C and by prolonging the reaction time up to 1 hour. Thereupon there were dosed off 0.0407 mols of unreacted hydrogen peroxide and 0.0805 mols of epoxycyclohexane, which corresponded to a conversion of the hydrogen peroxide of 68.4%, with a selectivity with respect to epoxycyclohexane of 91.1%.

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Example 18 (comparative example)

Example 17 was repeated, but the phosphoric acid was replaced by an equivalent quantity of H_2SO_4 . After 30 minutes of reaction, from the reaction mass were dosed off 0.00413 mols of epoxycyclohexane.

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Example 19 (comparative example)

Example 17 was repeated, but in the absence of $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ and by replacing the H_3PO_4 by 0.9 g (0.006 mols) of $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$. After 30 minutes of reaction, from the reaction mass there was dosed off a quantity of hydrogen peroxide equal to that introduced initially, and no presence of epoxycyclohexane was detected by LGC.

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Example 20

Example 13 was repeated, but using instead of $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ 2.42 g (0.010 mols) of $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ and by using 5.1 g (0.0077 mols) of 14.7% concentration H_3PO_4 . After 30 minutes of reaction, from the reaction mass were dosed off 0.1088 mols of unreacted hydrogen peroxide and 0.0010 mols of epoxycyclohexane, which corresponded to a conversion of the hydrogen peroxide of 15.6%, with a selectivity with respect to epoxycyclohexane of 49.5%.

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Example 21

Example 10 was repeated, but using instead of $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ and H_3PO_4 , 2.46 g of $2\text{Na}_3\text{PO}_4 \cdot 24\text{WO}_3 \cdot \text{H}_2\text{O}$ (sodium phosphotungstate) equal to 0.010 g-atom of W and to 0.0008 g-atom of P. To this reaction mass were then added 1.9 ml of 35% concentration NaOH. After 30 minutes of reaction, from the reaction mass were dosed off 0.0877 mols of unreacted hydrogen peroxide and 0.0245 moles of epoxycyclohexane, which corresponded to a conversion of the hydrogen peroxide of 32.1%, with a selectivity with respect to epoxycyclohexane of 59.3%.

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Example 22

Example 2 was repeated but using 2.42 g (0.010 mols) of $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ instead of $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ and by using 1,2-dichloroethane (60 ml) instead of benzene as a solvent. After 2 hours of reaction, from the reaction mass were dosed off iodometrically 0.1105 mols of unreacted hydrogen peroxide and 0.0081 mols of epoxyoctane, which corresponded to a conversion of the hydrogen peroxide of 14.3%, with a selectivity with respect to epoxyoctane of 43.8%.

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Example 23

Example 1 was repeated, but substituting the octene-1 with 33.35 g (0.1985 mols) of 1-dodecene. After 1 hour, from the reaction mass were dosed off 0.0059 mols of hydrogen peroxide and 0.0958 mols of 1,2-epoxydodecane, which corresponded to a conversion of the hydrogen peroxide of 91.9%, with a selectivity with respect to epoxydodecane of 80.7%.

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 H_2O_2 0.123 mol**Example 24**

Into an autoclave of 1 litre holding capacity, lined with glass and provided with a magnetic stirrer there were introduced 2.48 g (0.0075 mols) of $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$, 1.25 g (0.009 mols) of $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$, 2.9 ml (0.0044 mols) of 14.7% concentration H_3PO_4 , 0.25 ml of 31.7% concentration H_2SO_4 , 50 ml of 1,2-dichloroethane, 1.3 g (0.0032 mols) of tricaprylmethylammonium chloride, and 32.35 g (0.363 mols) of 38.2% concentration H_2O_2 .

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After removal of the air from the autoclave, into the latter were loaded 72 g of propylene (1.714 mols). The reaction mass was thereupon heated up to 60°C under vigorous stirring, thereby attaining a pressure of 18 atmospheres. The reaction mass was then maintained at this temperature for 1 hour. At the end of this period, after cooling down, there were dosed off 6.32 g (0.186 mols) of unreacted H_2O_2 and 6.73 g (0.116 mols) of propylene oxide, which corresponded to a conversion of the hydrogen peroxide of 48.76%, with a selectivity with respect of propylene oxide of 65.5%. Moreover, there were obtained 0.63 g (0.008 mols) of propylene glycol.

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CLAIMS

1. A process for the catalytic epoxydization of olefins by reaction with hydrogen peroxide according to the double phase technique with onium salts, wherein the reaction is conducted in a liquid aqueous-organic two-phase system which comprises (a) an organic phase substantially containing the olefin and (b) an aqueous acidic phase substantially containing the hydrogen peroxide, in the presence of a catalytic system

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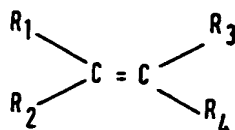
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comprising a first catalyst component which is at least one first element or a derivative thereof selected from tungsten, molybdenum and vanadium, and a second catalyst component which is at least one derivative of phosphorus or arsenic.

2. A process as claimed in Claim 1, wherein the reaction is conducted at a temperature of from 0°C to 120°C.

3. A process as claimed in Claim 1 or 2, wherein the reaction is conducted at a pressure of from 1 to 100 atm.

4. A process as claimed in any of Claims 1 to 3, wherein the olefin is represented by the formula



wherein R_1 , R_2 , R_3 and R_4 , optionally substituted with functional groups inert to the reaction conditions, each represent a hydrogen atom, or a hydrocarbyl group selected from alkyl and alkenyl groups having up to 30 carbon atoms, cycloalkyl and cycloalkenyl groups having from 3 to 12 carbon atoms, optionally branched, and aryl, alkyl-aryl and alkenyl-aryl groups having from 6 to 12 carbon atoms, and wherein, moreover, an R_1 , R_2 , R_3 , R_4 group taken together with an adjacent group may represent an alkyl or alkenyl group having up to 12 carbon atoms in the resulting cycle.

5. A process as claimed in Claim 4, wherein the inert functional group substituent of the olefin is at least one group selected from halogens, and hydroxyl, nitro, alkoxy, amino, carbonyl, carboxylic, esteric, amido and nitrile groups.

6. A process as claimed in Claim 4 or 5, wherein the olefin is selected from alkyl, alicyclic and alkylaryl unsaturated hydrocarbons having up to 20 carbon atoms, unsaturated alkyl halides, unsaturated acids and their esters, unsaturated alcohols and their esters, and unsaturated aldehydes and ketones.

7. A process as claimed in any of Claims 1 to 6, wherein the reaction is conducted at a pH value of from 2 to 6.

8. A process as claimed in any of Claims 1 to 7, wherein the quaternary onium salt is represented by the formula $(R'_1, R'_2, R'_3, R'_4M)^+X^-$, wherein M is a pentavalent element belonging to group VA of the Periodic System, X^- is an anion selected from Cl , Br , HSO_4^- and NO_3^- , and R'_1 , R'_2 , R'_3 and R'_4 each represent monovalent hydrocarbyl groups having a total number of carbon atoms of up to 70.

9. A process as claimed in Claim 8, wherein the said total number of carbon atoms is from 25 to 40.

10. A process as claimed in any of Claims 1 to 9, wherein the first catalyst component comprises at least one element or a mineral, organic or metalorganic derivative of the said element selected from tungsten, molybdenum and vanadium, capable of being transformed *in situ* under reaction conditions into a compound or a species catalytically active.

11. A process as claimed in Claim 10, wherein the said element is tungsten.

12. A process as claimed in Claim 10 or 11, wherein the first catalyst component is selected from the oxides, mixed oxides, oxyacids, homopolyacids and their salts, heteropolyacids and their salts, salts derived from mineral hydrogen acids, naphthenates, acetylacetonates and carbonyl derivatives of the elements W, Mo and V.

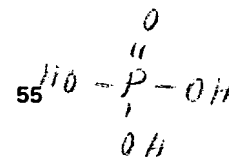
13. A process as claimed in any of Claims 10 to 12, wherein the first catalyst component is selected from W, Mo and V in the metal state, tungstic, molybdic and, vanadic acids and the corresponding neutral salts or acid salts of alkali or alkaline earth metals, the metal-carbonyls $W(CO)_6$, $Mo(CO)_6$, the oxides MoO_2 , Mo_2O_5 , Mo_2O_3 , MoO_3 , WO_2 , W_2O_5 , WO_6 , VO_2 , V_2O_3 , V_2O_5 , the sulphides WS_2 and WS_3 , the oxychlorides, the chlorides, the naphthenates and the stearates of molybdenum, tungsten and vanadium.

14. A process as claimed in any of Claims 1 to 13, wherein the second catalyst component comprises at least one mineral, organic or metalorganic derivative of phosphorus or arsenic, capable of forming, under reaction conditions, a catalytically active association with the first catalyst component as defined in any of Claims 10 to 13.

15. A process as claimed in Claim 14, wherein the second catalyst component is selected from oxides, oxyacids and their salts, sulphides and salts derived from hydrogen acids of phosphorus and arsenic, compounds of the formula $R''_1R''_2M(=O)X$ and $R''_3M(=O)XY$, wherein M is P or As and R''_1 , R''_2 , R''_3 each represent a hydrogen atom or an alkyl, cycloalkyl, aryl or alkylaryl group having up to 12 carbon atoms, and wherein X and Y each represent hydrogen, a halogen, or a hydroxyl, alkyl, aryl, aralkyl, alkoxy or carboxylic group, or a mineral oxyacid.

16. A process as claimed in Claim 14 or 15, wherein the second catalyst component is selected from phosphorous, phosphoric, polyphosphoric, pyrophosphoric, phosphonic, arsenious, arsenic and arsonic acids and their alkaline salts, the oxides P_2O_3 , P_2O_5 , As_2O_3 , As_2O_5 , the oxychlorides, the fluorides and the chlorides of phosphorus and arsenic.

17. A process as claimed in any of Claims 10 to 16, wherein the two or more catalyst components are part of one and the same complex molecule that incorporates them.



18. A process as claimed in Claim 17, wherein the two or more catalyst components are part of a derivative of a heteropolyacid selected from phosphotungstic, arsenotungstic and phosphomolybdic heteropolyacids and their alkali and alkaline earth salts.
19. A process as claimed in any of Claims 10 to 18, wherein the two or more catalyst components are used in a mutual atomic ratio expressed as the total of the metal or metals belonging to the first catalyst component with respect to the total of the metal or metals belonging to the second catalyst component of from 12 to 0.1.
20. A process as claimed in Claim 19, wherein the said atomic ratio is from 1.5 to 0.25.
21. A process as claimed in any of Claims 1 to 20, wherein the catalytic system is used in an amount of from 0.0001 to 1 g-atom of total metal or metals belonging to the first catalyst component per 1 mol of hydrogen peroxide.
22. A process as claimed in Claim 21, wherein the catalytic system is used in an amount of from 0.005 to 0.2 g-atom of total metal or metals belonging to the first catalyst component per 1 mol of hydrogen peroxide.
23. A process as claimed in any of Claims 1 to 22, wherein the catalytic system comprises mixtures of catalyzing elements and/or derivatives thereof.
24. A process as claimed in any of Claims 1 to 23, wherein the amount of quaternary onium salt used in the process is from 0.01 to 2 mols of onium salt per 1 g-atom of catalyst, relative to the first catalyst component or to the sum total of the first catalyst components.
25. A process as claimed in Claim 24, wherein the said amount of quaternary onium salt used is from 0.1 to 1 mol per 1 g-atom.
26. A process as claimed in any of Claims 1 to 25, wherein the onium salt is dicytyldimethylammonium chloride or tricaprylmethylammonium chloride.
27. A process as claimed in any of Claims 1 to 26, wherein the olefin is used in an amount with respect to the hydrogen peroxide of from 0.1 to 50 mols of olefin per 1 mol of hydrogen peroxide.
28. A process as claimed in Claim 27, wherein the olefin is used in an amount of from 1 to 20 mols per 1 mol of hydrogen peroxide.
29. A process as claimed in any of Claims 1 to 28, wherein the olefin concentration in the organic phase is from 5% to 95% by weight.
30. A process as claimed in any of Claims 1 to 29, wherein the hydrogen peroxide concentration in the aqueous phase is from 0.1% to 70% by weight.
31. A process as claimed in Claim 30, wherein the hydrogen peroxide concentration in the aqueous phase is from 1% to 10% by weight.
32. A process as claimed in any of Claims 1 to 31, wherein the organic phase comprises the starting olefin.
33. A process as claimed in any of Claims 1 to 32, wherein the solvent for the olefinic organic phase is an inert solvent substantially unmixable with the aqueous phase.
34. A process as claimed in Claim 33, wherein the solvent for the olefinic organic phase is selected from aliphatic, alicyclic and aromatic hydrocarbons, chlorinated hydrocarbons, alkyl esters and mixtures thereof.
35. A process as claimed in Claim 34, wherein the solvent for the olefinic organic phase is benzene or 1,2-dichloroethane.
36. A process according to Claim 1, for epoxydization of olefins substantially as herein described in any of the foregoing Examples 1 to 3, 5, 7 to 17, and 20 to 24.
37. An olefin epoxide obtained by the process as claimed in any of Claims 1 to 36.